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PATENT

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TO ALL WHOM IT MAY CONCERN:

Be it known that WE, EMILIO RODRIGUEZ CABEO, GÜNTHER LAUDIEN, KYONG-TSCHONG RIE, and SWEN BIEMER, citizens of Germany, whose post office addresses are: Eschenkamp 5a D-38550 Isenbüttel; Langes Moor 21, D-38542 Leiferde; Rostockerstrasse 14, D-38124 Braunschweig; and Echternstrasse, 17, D-38100 Braunschweig, Germany, respectively, have invented an improvement in

METHOD AND ARRANGEMENT FOR PLASMA BORONIZING

of which the following is a

SPECIFICATION

REFERENCE TO RELATED APPLICATION

This application is a continuation of International Application No. PCT/EP98/08079 filed December 11, 1998.

BACKGROUND OF THE INVENTION

This invention relates to methods and arrangements for producing a boride layer on a surface by plasma boronizing in which a gas mixture containing a boron-releasing gas is supplied to a reactor in which a glow discharge is generated.

The boronizing process, which belongs to the group of thermochemical methods of treatment, makes it possible to produce wear-resistant surface layers, preferably on

metal components, which provide excellent protection against high abrasive and adhesive wear stresses. Until now, industrial boronizing processes have frequently used solid boron-releasing media in the form of, for example, powders or pastes. However, such processes have a number of drawbacks which limit the production of borides to certain applications for which no alternative treatments that would provide a comparable wear resistance exist. These drawbacks include, for example, the high cost of manual handling of the materials used. In this regard, the component to be boronized must be packed in boron-releasing powder or the boronizing paste must be spread on the component, and the residual boronizing agent must be removed after completion of the boronizing. For ecological reasons, all residues of boronizing agent must be disposed of at suitable waste-disposal dumps. Frequently, the prior-art methods cannot be adequately controlled or cannot be controlled at all and automation of such processes is impossible.

For this reason, various methods have been developed for producing a boride layer on a surface by plasma boronizing in which a gas mixture containing a boron-releasing gas is supplied to a reactor and a glow discharge is generated within the reactor. Such a process is described, for example, in German Offenlegungsschrift No. 196 02 639. That publication discusses the problem of plasma boronizing of metal surfaces, for example, in which the resulting layers have a substantial porosity. Such porosity has a negative effect on the wear resistance of the boronized surface. Moreover, the plasma boronizing method as described in the aforementioned publication cannot be developed for industrial series applications.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method and arrangement for plasma boronizing which overcomes disadvantages of the prior art.

Another object of the invention is to provide a plasma boronizing method which produces substantially pore-free boronized surfaces in a reliable manner and is therefore suitable for industrial series applications.

These and other objects of the invention are attained by providing a boronizing method in which a gas mixture containing a boron-releasing gas is supplied to a reactor in which the gas releases boron in a glow discharge plasma and a glow discharge parameter is controlled to maintain the amount of at least one glow discharge product of the boron-releasing gas, or the relation of that amount to the amount of another glow discharge product, within selected maximum and minimum limits, or in which the glow discharge pulse ratio is maintained above a selected level, or the glow discharge pulse duration is maintained below a maximum value.

The invention further provides an arrangement for producing a boride layer on a surface by plasma boronizing including a reactor having a treatment chamber to which a gas mixture containing a boron-releasing gas is supplied and in which a glow discharge is generated by a DC voltage having a variable pulse width or pulse pause. This arrangement is suitable for carrying out the method of the invention in accordance with the abovementioned parameters, and will be described in detail hereinafter.

First, various alternatives for carrying out the method according to the invention will be described in greater detail. It has now been established by extensive testing that it is important in plasma boronizing to properly select the production parameters of the plasma generated in the treatment chamber of the reactor. It has surprisingly been found that these parameters can be selected advantageously in such a way that an increased proportion of excited boron particles is produced in the plasma. If the plasma contains a relatively large amount of excited boron, boron layers of low porosity will be produced. This fact was demonstrated by optical emission spectroscopy and plasma analysis during development work leading to the method of the invention. If, on the other hand, the plasma contains a high concentration of excited BCl particles, highly porous layers are produced which should be avoided for the abovementioned reasons. During the studies which resulted in the invention, the inventors established that various parameters with respect to both plasma generation and the individual components contained in the gas mixture supplies to the reactor can have an effect on the desired concentration of excited boron particles. It is important that, in order to obtain the desired boride layer of low porosity, certain threshold values of excited boron be attained in the plasma.

In accordance with one embodiment of the plasma boronizing method of the invention, a glow discharge is preferably generated with a pulsed DC voltage. In this connection, it was found surprisingly that control of the pulse-duty factor, which is defined as the ratio of the duration of the voltage pulse to the subsequent pulse pause before the next voltage pulse, facilitates the desired production of an increased

concentration of excited boron particles and thus facilitates optimum control of the plasma generation method. According to one variation of the method of the invention, the pulse-duty factor should be greater than 1.1:1, preferably in the range from 1.25:1 to 5:1, and desirably in the range from 1.5:1 to 3.5:1. Furthermore, the pulse period, which is the sum of the durations of the voltage pulse and pulse pause, is preferably less than about 230 μs, but $\geq$ 50 μs.

Desirably, the pulse period is less than about 230 μs and more than 50 μs, for example, about 210 μs. According to one embodiment of the method of the invention, the DC voltage used for the pulsed current to produce the glow discharge is preferably in the range between about 500 volts and about 1000 volts, desirably in the range between about 600 volts and about 900 volts, and more desirably in the range between about 650 volts and about 800 volts. It was further found that, when working with higher voltage, the use of a longer pulse pause is advantageous. However, a good result is also achieved when applying lower voltage, preferably within the abovementioned voltage ranges, but even in this case, the composition of the individual components of the gas mixture supplied to the reactor can exert an influence on the resulting coating characteristics.

In the method of the invention, it is preferable to use, as a first component of the gas mixture supplied to the reactor, a boron-releasing gas in the form of a boron halide, for example, boron trichloride or boron trifluoride. Preferably used as second component of the gas mixture is hydrogen gas, and optionally, as third component of the gas mixture, a noble gas such as argon. It has been found that, when using argon as a third component

in the method of the invention, good boride layers can be obtained even when applying relatively low voltages.

The concentration of boron trihalide as a boron-releasing gas in the gas mixture generally has an effect on the boride layer produced by the method. In general, the boron trihalide content should not be too low and, as rule, should not be less than 1% by volume, since otherwise a suitable boride layer may not be obtained. In accordance with one embodiment of the method of the invention, the boron trihalide content is preferably in the range of about 2% by volume to 50% by volume. It should be noted, however, that excessively high boron trihalide contents cause a relatively high boron trihalide loss. The lost boron trihalide is contained in the waste gas from the reactor and results in high cost for waste gas disposal or purification. Especially good results have been obtained with the process of the invention when a boron trihalide content preferably in the range between about 2% by volume and 10% by volume, for example, about 7.5% by volume of boron trihalide, is used. If a noble gas is used as a third gas mixture component in the method of the invention, then the content of the noble gas, for example, argon, is preferably in the range between about 0% by volume and about 20% by volume. The second component of the mixture is preferably hydrogen gas in an amount corresponding to the remainder of the gas mixture content using the above-specified preferred ranges of the other two components, i.e. the boron trihalide and the noble gas.

The method according to the invention is preferably carried out at a low pressure, for example, a pressure in the range between about 0.5 and about 15 hPa, desirably in a range between about 1 and 10 hPa.

The selection of the desired method parameters for achieving the desired coating characteristics can be achieved, for example, in such a way that the amount of excited boron particles in the plasma is determined analytically and one or more process parameters are changed appropriately to generate the glow discharge parameters such as voltage, pulse duty factor, frequency, temperature, pressure, etc., which produce the desired result.

According to one embodiment of the method of the invention, the boride layer can be produced in several stages, in which case, for example, the coating is carried out at a relatively low treatment temperature during a first stage in order to reduce halide formation in the plasma which is partially responsible for pore formation. In this first stage, a relatively thin but pore-free boride layer is produced which is more resistant to corrosive attack. Subsequently, in a second stage, the treatment temperature is raised in order to enhance the diffusion of the boron particles and thus the formation of a layer of increasing thickness. Even when a parameter such as, in this case, the treatment temperature, is changed in such a two-stage or optionally multistage process, care should be taken that the other process parameters are controlled so that, if possible, an increased content of excited boron particles is obtained in the plasma in order to enhance the boron coating reaction and avoid a corrosive attack.

It has been found that, in the method of the invention, adjustment of the current passing through the plasma generally has a considerable effect. The influence exerted on the layer characteristics and the suppression of pore formation caused by the chlorine components present in the treatment atmosphere, and the enhancement of boride formation, as two reactions competing with one another, are determined by these and other plasma parameters. Depending on the pulse duty factor and the gas composition it is possible, by adjusting the voltage in a specified manner, to obtain a plasma condition characterized by a high particle density of boron-releasing components, so that boride formation preferentially takes place. Analysis of the plasma composition can be carried out, for example, with the aid of optical emission spectroscopy. In this connection, it has been found that the signals for the excited boron, the excited BCl and the Cl^+ signal, in particular, can be used for optimizing the layer characteristics. Those methods of carrying out the invention in which the analysis shows high B signals were found to be favorable. This is possible, for example, with voltages within an average range of preferably about 650 volts to about 800 volts, where the boron trihalide content of the gas mixture and the pulse-duty factor of the pulsed DC voltage play an additional role.

The method of the invention is suitable for industrial uses and can be developed to a point where it is ready for series production. Compared with prior art boronizing methods of the kind discussed above, which operate with solid boron dispensing media, plasma boronizing with a gaseous boron-releasing dispensing medium has an enormous improvement potential. Handling of the components to be treated can be reduced to a

minimum. The method of the invention is suitable for automation. By changing the treatment time, it is possible according to the method of the invention to change the gas composition so that an effect can thereby be exerted on layer formation, in which case special care should be taken to avoid the formation of FeB. Furthermore, the method according to the invention takes environmental considerations into account since any residues of boronizing agent to be disposed of can be minimized.

Areas of industrial application of the method according to the invention are, for example, boronizing of metal parts to increase the wear resistance of the surfaces of components which are exposed to particularly high abrasive or adhesive stresses. The method according to the invention is suitable, for example, for boride layer application to components in the automobile industry, for example for gears, hydraulic plungers, camshafts, oil pump drives, for example, with crossed axes, helical gear wheels, and also for extruder screws and other components exposed to high stress.

The arrangement for the production of a boride layer on a surface by plasma boronizing according to the invention includes a reactor to which a gas mixture containing a boron-releasing gas can be supplied and in which a glow discharge plasma is generated. The boronizing arrangement has a plasma generator which furnishes a pulsed DC voltage with a controllable pulse width and/or pulse pause.

1. The arrangement according to the invention preferably has at least one mass flow meter for measurement and/or adjustment of the composition of the gas mixture and/or the flow rate of one or more of the gases in the gas mixture. In this way, the

instantaneous composition of the gas mixture supplied to the reactor can be measured at any time, and thereupon the composition of the gas mixture and/or the supply of one or more of the gases contained in the gas mixture can be changed. In this way, it is possible to exert an influence on the process. For example, by changing the composition of the gas mixture during the process, the layer formation may be altered, optionally as a function of the analytical results of the determination of the particle composition in the plasma. The method is preferably carried out with a gas mixture containing two or three components, for example, a boron trihalide, hydrogen and a noble gas. Hence, three mass flow meters are preferably included, one for the measurement and/or adjustment of the supply of each of the three components, respectively,

Preferably a pressure gauge which is independent of the type of gas is used for measurement of the treatment pressure. The pressure gauge is preferably computer-controlled.

The gases are distributed into the treatment chamber of the reactor, for example, by a gas sprayer.

Furthermore, in the case of a thermally decomposable boron-releasing gas, it has been found advantageous to use a cooled gas inlet, since, in that way, the boron-releasing gas can be more effectively utilized.

Moreover, in a further development of the invention, it is advantageous for environmental reasons to use a gas purification device for treatment of waste gas in order to minimize the amount of boron in the waste gas and thus minimize the environmental

damage of the method. For this purpose, for example, an arrangement in which the gas purification device is attached to a vacuum pump for reducing the pressure in the treatment chamber can be used can be used.

In a further embodiment of the invention, the reactor may contain an additional heating device to achieve the desired treatment temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

Further objects and advantages of the inventions will be apparent from a reading of the following description in conjunction with the accompanying drawings, in which:

Fig. 1 is a schematic diagram illustrating a representative embodiment of an arrangement for producing a boride layer on a surface by plasma boronizing according to the invention; and

Fig. 2 is a graphical representation showing the variation, as a function of time, of the voltage for the pulsed DC voltage used in an embodiment of the method according to the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the schematic representation of a typical embodiment of an arrangement for carrying out the method of the invention for producing a boride layer on a surface by plasma boronizing shown in Fig. 1, a reactor **10** has a treatment chamber **11** wherein a plasma is generated. The treatment chamber **11** of the reactor **10** is charged with a gas

mixture containing a boron-releasing gas which is introduced into the treatment chamber **11** through a gas inlet **12** and a supply line **13**. Attached to the supply line **13** are three feed lines through which the individual components of the gas mixture are introduced. One of the components is the boron trihalide, for example, boron trichloride or boron trifluoride, which is supplied through a branch line **14** which opens into the supply line **13**. The second component is hydrogen gas supplied through a branch line **15** which likewise opens into the supply line **13**. The third component is a noble gas, for example, argon, which is fed through a branch line **16** which also opens into the supply line **13**. Three flow meters **17, 18** and **19** are provided in the feed lines **14, 15** and **16**, respectively, of which the throughput of each of the components of the treatment gas mixture can be adjusted and measured.

The reactor **10** further includes a charging plate **20** supported in the reactor chamber **11** on two rod insulators and a flow-guiding support (not shown). The voltage for generating the glow discharge is provided through a schematically shown voltage feed line **21.** The plasma generator provides a pulsed DC voltage with a controllable pulse width and pulse pause, as explained hereinafter.

The composition and throughput of the treatment gas mixture are adjusted by controlling the mass flow meters **17, 18** and **19**. The treatment pressure is measured by a pressure gauge that is independent of the type of gas and is controlled by a computer. The measurement of pressure and control of the pressure are effected by a pressure control device **22** which is connected to the treatment chamber **11** through a line **23**. Connected

to this line after the pressure control device **22** is a vacuum pump **24** and connected to the vacuum pump **24** in this line is a device **25** for waste-gas purification, which provides for adequate waste-gas treatment as waste gases are withdrawn from the treatment chamber **11**.

The temperature of the plasma generator is controlled by a temperature control device **26** and a control line **27**.

Furthermore, the arrangement according to the invention has an additional heating device **28** which is provided in the reactor **10** to establish the desired treatment temperature in the treatment chamber **11**.

The method of the invention for producing a boride layer preferably is carried out at a low pressure, for example, in the range of 1 to 10 hPa, and is supported by electric activation of the gas atmosphere. The components to be boronized are cathodically connected to the container wall of the treatment chamber. The gas mixture, preferably containing a boron trihalide, for example, boron trichloride or boron trifluoride, hydrogen and noble gas, is introduced into the treatment chamber **11** and, in addition to thermal activation, undergoes electric activation to produce a through the glow discharge. The treatment temperature depends on the material of the respective components to be boronized and is, for example, above 700°C, preferably 800°C or higher.

A pulsed DC voltage is preferably applied in order to facilitate activation of the surface by the noble gas/ion bombardment prior to the treatment phase. Beyond that, during the treatment, active excited boron particles are produced which reach the surface

of the component where they primarily form borides by diffusion. The reduction of the halogen present in the atmosphere produced from the boron trihalide is enhanced by the atomic hydrogen produced in the plasma from the H_2 gas supplied to the chamber.

The diagram of Fig. 2 shows, by way of example, a representative voltage variation as a function of time for a pulsed direct current that is particularly advantageous for a method according to the invention. The voltage represented is, for example, in a middle range at 650 volts, with the voltage pulse maintained for 160 μs, for example, and the pulse pause maintained for 50 μs, for example. Thus, the pulse pause is shorter by a factor of 3 than the duration of the DC voltage pulse. The pulse period in this embodiment is 210 μs, and thus the frequency is 4.762 kHz. In this embodiment, the pulse-duty factor, defined as the ratio of the pulse duration to pulse pause within a pulse period is 3.2. It has been established that, when using a relatively high voltage, a longer pulse pause is required. However, when using argon in the treatment gas, good results can be achieved even at relatively low voltages, for example, in the range above 500 volts.

Although the invention has been described herein with reference to specific embodiments, many modifications and variations therein will readily occur to those skilled in the art. Accordingly, all such variations and modifications are included within the intended scope of the invention.